# Dynamic Light Scattering from the Oriented Lamellar State of Diblock Copolymers: The Undulation Mode

**Petr Štěpánek***

*Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic*

**Frédéric Nallet**

*Centre de recherche Paul-Pascal, CNRS, avenue du Docteur-Schweitzer, F-33600 Pessac, France*

**Kristoffer Almdal**

*The Danish Polymer Centre, Department of Solid State Physics, Risø National Laboratory,*
*P.O. Box 49, DK-4000 Roskilde, Denmark*

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ABSTRACT: Using a fully oriented sample of a diblock copolymer, poly(dimethylsiloxane)-*block*-poly(ethylene-*co*-propylene), we have observed, by dynamic light scattering, the undulation mode of the block copolymer lamellae in the ordered phase. This mode is observable only in a particular geometry where the scattering vector is parallel to the lamellar structure. From the relaxation frequency of the undulation mode, the splay elastic modulus, *K*, of the lamellar structure is derived. It is shown that the elastic modulus *K* extrapolates to zero near the order-to-disorder temperature where the translational long-range order disappears. The "fast" mode usually observed in block copolymer melts on disoriented samples presumably corresponds to the undulation mode in an oriented sample, averaged over all possible orientations.

## Introduction

Below the order-to-disorder transition (ODT), diblock copolymers AB form a variety of structures, the morphology of which depends mainly on the relative chain length of the two blocks. In particular, when the two blocks are of approximately equal length, the structure formed is lamellar with A and B blocks arranged in alternating layers, the normal to these layers pointing in a common direction $z$. Such a structure is similar to the smectic A phase existing in thermotropic (usually single-component and low-molecular-weight compounds) or lyotropic (two-component, surfactant−solvent mixtures) liquid crystals.

The dynamics of smectic A liquid crystals has been developed theoretically by de Gennes,[1] who predicted in particular that the undulation mode of smectic layers should be easily observable by light scattering. The undulation mode corresponds to a deformation of the layers with no alteration in the interlayer distance. In comparison with other collective layer displacement modes, second sound for instance, undulation deformations require little energy and have large amplitudes.

To observe the undulation mode with light scattering, a geometry must be chosen where the scattering vector $\mathbf{q}$ lies in the plane of the smectic layers, i.e., $q_z = 0$. When this condition is not satisfied, the interlayer distance departs from its equilibrium value, and the second sound mode is generically observed in the case of single-component smectics[1] or the baroclinic mode with lyotropic systems.[2,3]

Experimentally, the dynamics of lyotropic smectic A liquid crystals has been studied using dynamic light scattering in various systems.[3−5] Two elastic constants have been extracted from the measurements, namely the layer-compression modulus $\bar{B}$ and the splay modulus $K$. The former—related to the baroclinic mode relaxation frequency—is obtained when the wave vector is oblique ($q_z \neq 0$), the latter, which controls layer undulations, for $q_z = 0$.

Dynamic light scattering was also used much earlier to study the undulation mode in thermotropic liquid crystals by Ribotta et al.[1] in a smectic A phase and by Birecki et al.[2] near a smectic A-to-nematic transition. In these pioneering works, $K$ as well as $\bar{B}$ is measured from the detailed, quantitative analysis of the undulation mode dispersion relation in the close vicinity of the optimum setting $q_z = 0$. This is the method we follow in the present contribution where we report the first observation of the undulation mode in the lamellar phase of a diblock copolymer.

## Theory

Lamellar block copolymer melts are smectic materials in the sense in which this term is used in liquid crystals. They satisfy indeed the principles of structure and symmetry of smectics:[8] (i) equidistant layers, with period $d$, which are perpendicular to a given direction Oz; (ii) no long-range order within individual layers; (iii) no privileged direction in the plane of the layers, i.e., the system is optically uniaxial with axis Oz; (iv) directions +Oz and −Oz are equivalent (no ferroelectricity).

The number of relevant hydrodynamic variables can be obtained[9] by counting the number of locally conserved quantities and continuously broken symmetries. The usual five variables of a simple fluid are the total mass density $\rho$, the momentum density $\mathbf{g}$, and the energy density $\epsilon$. In the case of single-component smectics, a sixth variable is introduced, the layer displacement $u$, associated with the loss of translational symmetry along the normal to the layers. Six hydrodynamic modes thus have to be considered, namely: heat diffusion (one

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mode), shear (one mode), sound (two modes), second sound (two modes). A complete mathematical description of these modes involves six coupled equations.[9] This number can be reduced by some assumptions: if the system is assumed incompressible and athermal, three equations can be replaced by constrains on pressure, longitudinal momentum, and temperature. This approximation is valid for any mode with a frequency smaller than the sound frequency (typically 2 GHz at $q \sim 10^7$ m$^{-1}$) and the thermal mode relaxation frequency ($\sim$1 MHz). Of the three equations that remain, one is uncoupled. It describes a transverse (with respect to both wave vector and optical axis) shear wave with a high frequency (in the terahertz range at $q \sim 10^7$ m$^{-1}$, owing to the very large viscosity of polymeric material); it couples little to layer displacement fluctuations and thus scatters light very weakly. The equation is not of interest in the context of the present work. The remaining two coupled hydrodynamic equations are

$$\partial_t g_t = -\frac{\eta}{\rho} q^2 g_t + (\bar{B} q_z^{\,2} + K q_x^{\,4}) \frac{q_x}{q} u$$

$$\partial_t u = -\frac{q_x}{\rho q} g_t \qquad (1)$$

In eq 1, the $x-z$ plane contains both the wave vector $\mathbf{q}$ and the normal to the layers (along the $z$-direction), $g_t$ is the transverse momentum, and $\eta$ is a shear viscosity (for simplicity, the viscosity tensor is assumed isotropic). Note also that permeation[10]—presumably an extremely slow process in the present context—is neglected.

In the limiting case of $q_z = 0$, the solution of eq 1 leads to two modes: a shear mode which is not of interest here and the undulation mode, which has a relaxation frequency given by

$$\Gamma_u = \frac{K}{\eta} q_x^{\,2} \qquad (2)$$

in the usual limit where $K\rho/\eta^2 \ll 1$.

The frequency of this mode is typically 10 kHz; it couples strongly to layer displacement fluctuations and should thus be easily observable in light scattering.[1]

For an oblique $\mathbf{q}$ vector, $q_z \cdot q_x \neq 0$; the solution of eq 1 is more complex. In the immediate vicinity of $q_z = 0$, the shear-related mode may still be considered of a much higher frequency than the undulation-related mode, and the adiabatic approximation $\partial_t g_t \approx 0$ should be still valid. We thus obtain for the low-frequency mode

$$\Gamma_u = \frac{\bar{B} q_z^{\,2} + K q_x^{\,4}}{\eta} \frac{q_x^{\,2}}{q^4} \qquad (3)$$

where it can be easily verified that, for $q_z = 0$, eq 3 transforms into eq 2.

## Experimental Section

**Sample Preparation.** The diblock copolymer used for this work was poly(dimethylsiloxane)-*block*-poly(ethylene-*co*-propylene) (PDMS−PEP), synthesized by anionic polymerization as described elsewhere.[11] The molar mass of the polymer is $M_n = 6300$ g/mol, and the fraction of PEP monomers is $f_A = 0.48$. This copolymer has an ODT transition[11] at $T_{ODT} = 64$ °C. It is well-suited for dynamic light scattering experiments (DLS) because it has a relatively low molar mass and thus also a low viscosity. After a change in temperature, structural equilibrium can be reached in a reasonable time, and relaxation rates are well within the time window of the DLS technique.

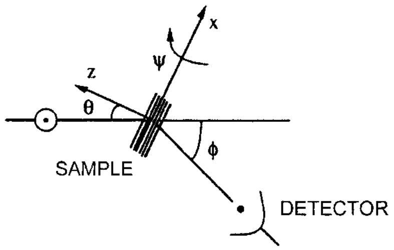

**Figure 1.** Geometry of the setup, drawn in the scattering plane. The angle $\phi$ controls the modulus of the wave vector; the angle $\theta$ controls the orientation of the smectic layers with respect to the scattering vector. The $z$-axis is the projection in the scattering plane of the normal to the layers. The angle $\psi$ controls the out-of-plane orientation of the smectic optical axis. The incident light is always polarized perpendicularly to the scattering plane.

The essential condition for experimental studies of lamellar block copolymers along the lines introduced above is the preparation of a sufficiently large "single crystal" of the ordered block copolymer, free of any defects. Normally, when cooling a block copolymer material from its high-temperature disordered phase into the low-temperature ordered lamellar phase, a "polycrystalline" structure is obtained: the copolymer is arranged in individual grains, each having a typical size of 1−3 μm, depending on the rate of cooling.[12] Each grain has an inner lamellar structure; thus, it is a small uniaxial single crystal, but mutual orientation of the grains is random with lots of defects at the boundaries of the grains.

The single crystal needed for the present work was prepared in a flat capillary of cross section 1 mm × 100 μm (VitroCom). The polymer was introduced by capillary forces at a temperature above the ODT, and the capillary was then sealed. The capillary was placed on the heating stage of an optical microscope. Orientation of the copolymer in a single crystal was achieved by repeated heating and cooling cycles with a rate of 0.01 °C/min in a temperature interval of about 1 °C around the ODT, observing the quality of orientation by polarized microscopy. Once the orientation was achieved, the capillary was slowly cooled to room temperature with a rate of 0.1 °C/min.

**Light Scattering Setup.** A customized light scattering instrument (Brookhaven Instruments) equipped with an additional rotary stage was used. The position of the detector (carried by a standard goniometer) is identified by the scattering angle $\varphi$ with respect to the direction of propagation of the incident laser beam. Two additional angles, $\theta$ and $\psi$, define the orientation of the optical axis of the sample (which is perpendicular to the block copolymer lamellae), as shown in Figure 1: (i) the angle $\theta$ describes the in-plane rotation of the rectangular cell around an axis perpendicular to the scattering plane (realized by the rotary stage to which is attached the sample holder); (ii) the angle $\psi$ measures the out-of-plane rotation around an axis parallel to the scattering plane (realized by using sample holders where the capillary is mounted in a fixed, tilted position).

The incident light is always polarized perpendicularly to the scattering plane (polarization vector $\mathbf{i}$). The undulations of smectic layers correspond to fluctuations in the direction of the local optical axis and are thus best observed in depolarized geometry. Therefore, the analyzer was always oriented parallel to the scattering plane (polarization vector $\mathbf{f}$).

The angle $\psi$ was chosen to be 25°. It must be different from 0 (i.e., the capillary must not be positioned vertically); otherwise, the undulation mode cannot be detected. Indeed, the intensity of light scattered by smectic layers is given by

$$I(\mathbf{q}) = \langle|\mathbf{i}\cdot\Delta\epsilon(\mathbf{q})\cdot\mathbf{f}|^2\rangle = \Delta\epsilon^2 (f_z \mathbf{i}\cdot\mathbf{q}_\perp + i_z \mathbf{f}\cdot\mathbf{q}_\perp)^2 \frac{k_B T}{\bar{B} q_z^{\,2} + K q_\perp^{\,4}} \qquad (4)$$

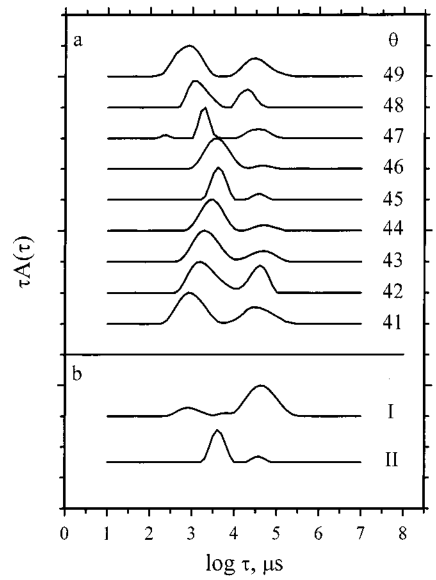

**Figure 2.** (a) Relaxation time spectrum, as a function of the angle $\theta$ (see text), for an *oriented* block copolymer sample in its lamellar state. The light scattering data are taken at $T$ = 26 °C for a scattering angle $\varphi = 90°$. Two modes—the undulation mode, with a strong anisotropy and small relaxation times, and the heterogeneity mode, at longer times and little anisotropy—may be observed. (b) Comparison between the relaxation time spectra for disoriented—I, $\varphi = 90°$—and oriented—II, $\theta = 45°$, $\varphi = 90°$—samples of the same material at temperature $T$ = 26 °C. The heterogeneity mode is observed at about the same relaxation time ($\log \tau \approx 4.5$) in both spectra I and II. The undulation mode appears on spectrum II at shorter relaxation times, and the "fast" mode (labeled $D_X$ in a previous work[15]) appears on spectrum I.

with $\Delta\epsilon$ the dielectric permittivity anisotropy: when $\psi = 0$, the optical selection rule term identically vanishes since $i_z$ and $\mathbf{i}\cdot\mathbf{q}_\perp$ both vanish.

The capillary with the desired orientation is surrounded by an index-matching liquid (decalin) contained in a glass vat. Assuming perfect matching, and even though the sample cell has a rectangular cross section, we neglect refraction for computing the magnitude of $\mathbf{q}$ and $q_z$. With $n$ the refractive index of the sample, we get

$$q = \frac{4\pi n}{\lambda} \sin \varphi/2$$

$$q_z = q \cos \psi \sin(\theta - \varphi/2) \qquad (5)$$

where $\lambda$ is the wavelength in vacuo of the incident radiation.

The dynamic light scattering setup is equipped with a BI 9000 correlator (Brookhaven Instruments) and a Kr$^+$ laser (Coherent) operated at a wavelength of 647.1 nm. The temperature of the sample is controlled using a standard water bath that ensures stability of the selected temperature with a precision of 0.1 °C. The correlation functions are analyzed using a Laplace inversion program[13] REPES, which is similar to the well-known program[14] CONTIN except that it fits directly the intensity correlation function $g_2(t)$ instead of fitting the field correlation function $g_1(t)$. A distribution of decay times is thus obtained from the measured intensity correlation function $g_2(t)$ according to the relation

$$g_2(t) - 1 = \alpha[\int A(\tau) \exp(-t/\tau)\, d\tau]^2 \qquad (6)$$

## Results

For a first series of measurements, the scattering angle $\varphi = 90°$ was selected. The condition $q_z = 0$ is then satisfied for $\theta = 45°$. Figure 2a shows distributions of decay times obtained at 26 °C for $\theta = 45°$ ($q_z = 0$) and a few other angles $\theta$ slightly smaller and larger than 45°. At $q_z = 0$, the correlation function is almost single-exponential, producing a distribution of decay times $A(\tau)$ with one dominant peak. A second weak component with decay time about an order of magnitude larger is present in this distribution. With increasing difference of the angle $\theta$ from 45° the relative amplitude of the fast component decreases.

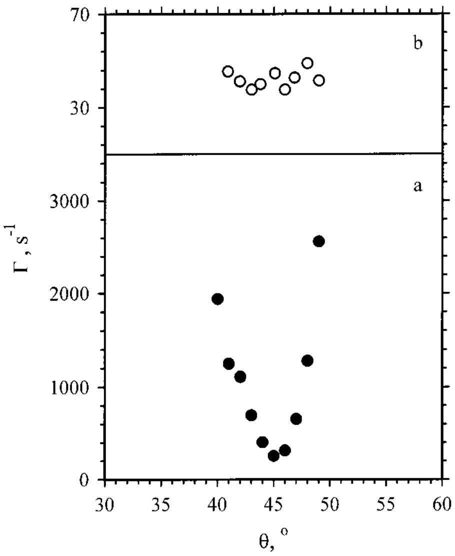

**Figure 3.** (a) Anisotropy of the relaxation frequency of the undulation mode as a function of $\theta$ for an oriented block copolymer sample in its lamellar state. The light scattering data are taken at $T$ = 26 °C for a *fixed* scattering angle $\varphi$ = 90°. (b) Similar to (a) for the heterogeneity mode, displaying very little anisotropy.

For comparison, Figure 2b shows dynamic light scattering results obtained in a previous work on another sample of the same block copolymer sealed *disoriented* in a round cell.[15] It was established there, using light scattering and PFG-NMR techniques, that the component located at $\log \tau \approx 4.5$ (curve I) corresponds to the heterogeneity mode governed by the self-diffusion of the block copolymer chains. Comparing the two curves in Figure 2b, we conclude that the slower weak mode obtained at $q_z = 0$ in the present measurements (curve II) corresponds to the heterogeneity mode. The origin of this mode is self-diffusion of the block copolymer chains, but it can only be seen because of the inherent heterogeneity in composition, i.e., the difference in composition of the individual chains. The light scattering amplitude of the heterogeneity mode would vanish[16] if all block copolymer chains (AB) had identical composition (identical fractions of monomer A, $f_A$). This mode is not contained in de Gennes' classic description of smectic systems, which is designed for single-component systems, i.e., systems made of identical molecules.

The undulation mode predicted by the theory is then the fast mode observed at $q_z = 0$. Its decay rate $\Gamma_u = 1/\tau$ is also strongly dependent on the angle $\theta$ as predicted in eq 3 and shown in Figure 3a. As $q_z$ departs from 0, the undulation mode very rapidly merges with the oblique second sound mode which leads to a 10-fold increase in relaxation frequency of the fast mode over the narrow angular range of typically 5° around $\theta = 45°$. Beyond this range of angles, the undulation mode cannot be reliably extracted from the correlation function since its amplitude becomes very small in agree-

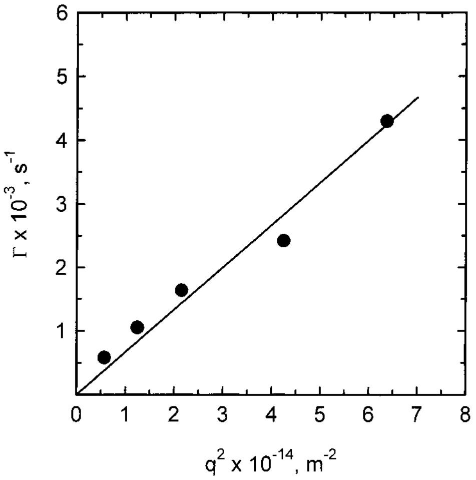

**Figure 4.** Relaxation frequency of the undulation mode, taken at $q_z = 0$, as a function of $q^2$. The slope gives the value for $K/\eta$ at $T = 26$ °C; see text.

ment with theoretical prediction (de Gennes' criterion[1] $q_z/q < 10^{-3}$ corresponds here to $\theta - \varphi/2 < 1°$); cf. also eq 4. In addition, the correlation function is then dominated by the heterogeneity mode. For completeness, Figure 3b shows that the relaxation rate of the heterogeneity mode does not depend, within experimental errors, on $\theta$ as expected since the dynamics of this mode should not depend *singularly* on $q_z$.

Measurements similar to those shown in Figure 3a have been repeated with other scattering angles $\varphi$, and similar results have been obtained, with the relaxation rate of the undulation mode being *minimum* for $q_z = 0$. Figure 4 shows the dependence of the relaxation rate $\Gamma_u$ obtained at $q_z = 0$ as a function of the square of the scattering vector. Within experimental errors, the data are compatible with a linear dependence passing through the origin. The data can thus be described by eq 2, $\Gamma_u = K/\eta q^2$ with $K/\eta = 5.96 \times 10^{-13}$ m$^2$ s$^{-1}$.

To obtain an estimate of the viscosity of the polymer, we extrapolate the viscosity data as a function of temperature for this sample in the *disordered* phase.[11] To justify this procedure, we refer to results of ref 17, where it has been shown for a polymer system having a lamellar phase at low temperatures that the temperature dependence of the Leslie viscosity $\eta$ in the ordered phase is the same as the temperature dependence of the viscosity $\eta_d$ in the disordered phase. Besides this, a reduction of viscosity from $\eta_d$ to $\eta$ due to lamellar organization was observed at ODT, of magnitude about 50%. Performing the extrapolation and applying the above-mentioned reduction of 50% gives, at 26 °C, $\eta = 10.4$ Pa·s. With this input number and the light scattering value for $K/\eta$ given above, we arrive at a value of the splay modulus, $K = 0.62 \times 10^{-11}$ N. This is in good agreement with the typical value of $K$ theoretically estimated in ref 18, namely $K \approx 10^{-6}$ dyn, i.e., $K \approx 10^{-11}$ N.

We have also measured the temperature dependence of the undulation mode relaxation frequency for a fixed value of the scattering angle $\varphi = 60°$. To minimize the risks of destroying the single-crystal structure, the temperature was changed very slowly, at a rate of 1 °C/h. Using the extrapolated viscosity, as before, we have extracted from the data the splay elastic constant $K$. Its temperature dependence is plotted in Figure 5. The dependence is approximately linear in the measured temperature range (22–50 °C), with a small, but significant, upward curvature. Fitting the data to a quadratic polynomial, we extrapolate from the measured temperature range to $K = 0$ and find that $K$ vanishes at $T = 74$ °C, about 10 °C above the ODT temperature.

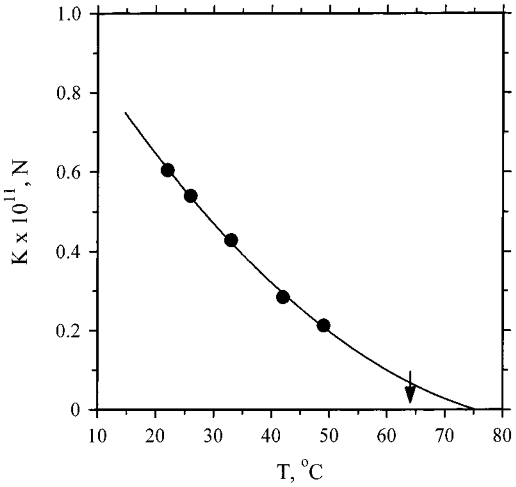

**Figure 5.** Temperature variation of the splay modulus $K$ for a measurement taken at the scattering angle $\varphi = 60°$. The arrow indicates the ODT, at temperature $T = 64$ °C. The line is a quadratic fit to the data. It extrapolates to zero about 10 °C above $T_{ODT}$.

## Discussion

The vanishing of the extrapolated elastic constant of the undulation mode at a temperature close to, but above, the point where the long-range lamellar structure itself disappears (as determined, e.g., by birefringence measurements[15]) is an additional indication that the fast mode in Figure 2 is indeed the undulation mode. In ref 18, Amundson and Helfand give a theoretical description of the mechanical properties of lamellar block copolymers. The ordering is described in the weak segregation limit, with the order parameter taken as a simple sinusoid $\psi = 2A \cos(q_0 z)$ of amplitude $A$ and wave vector $q_0$ for the undistorted state. Expanding to the first relevant order the free energy difference between a distorted state and the reference one, Amundson and Helfand obtain expressions for the two elastic constants $\bar{B}$ and $K$. In particular, the splay modulus $K$ is predicted to vary as[18]

$$K = 3.6426 \rho_c k_B T R_g{}^2 A^2 \tag{7}$$

with $\rho_c$ the number density of the polymer chains and $R_g$ the radius of gyration. Moreover, it is also shown in ref 18 that the degree of segregation between the two blocks—as measured by the amplitude $A$ of the order parameter below the ODT—decreases, approximately linearly, with increasing temperature and discontinuously jumps to zero at the metastability limit of the ordered phase.

We show in Figure 6 the calculated value for $A$, using eq 7, and our light scattering data for the splay modulus $K$. The temperature dependence of the number density $\rho_c$ is estimated from the polymer mass density $\rho = 0.95$ g/cm$^3$, its temperature dependence $d(\ln \rho)/dT = -0.0007$ K$^{-1}$ (data from ref 19), and the molar mass $M = 6300$ g/mol. We have used temperature-dependent values for $R_g$ calculated from the experimentally determined tem-

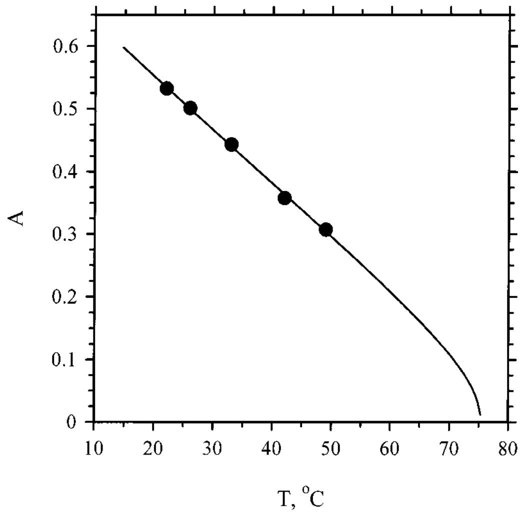

**Figure 6.** Temperature dependence of the amplitude $A$ of the order parameter (see eq 7). The line represents the transform through eq 7 of the quadratic fit displayed in Figure 5.

perature dependence of the end-to-end distance $\langle r^2\rangle_0^{0.5}$ of this copolymer, d $\ln\langle r^2\rangle_0^{0.5}/\mathrm{d}T = -0.25 \times 10^{-3}\ \mathrm{K}^{-1}$, and the relation $R_g = (\langle r^2\rangle_0/6)^{0.5}$ with[19] $\langle r^2\rangle_0^{0.5} = 9.3$ nm at $T = 100°$ C. It can be observed in Figure 6 that both the values for $A$ and the quadratic fit to our data for $K$, transformed through eq 7, are nicely compatible with the theoretical prediction.[18] We wish to point out that only experimentally determined quantities have been used in constructing Figure 6, with no adjustable parameters.

Returning now to Figure 2b, we observe that the position of the fast mode on curve I, obtained on a "polycrystalline" sample, differs by about a factor of 3 from the position of the relaxation time of the undulation mode in the *oriented* sample (curve II). This probably results from the strong anisotropy of the undulation mode dispersion relation predicted by eq 3 and experimentally observed in Figure 3, in combination with the (depolarized) scattering intensity anisotropy (cf. eq 4). Indeed, with Θ and Φ the polar coordinates localizing the direction of the normal to the smectic layers respective to the scattering vector **q** and $\varphi$ the scattering angle, eq 3 may also be written as

$$\Gamma_u = \frac{Kq^2}{\eta}\left(\sin^4\Theta + \frac{\bar{B}\cos^2\Theta}{Kq^2}\right)\sin^2\Theta \qquad (8)$$

and eq 4

$$I = \Delta\epsilon^2\frac{k_BT}{Kq^2}\frac{\sin^2\Theta}{\sin^4\Theta + \dfrac{\bar{B}\cos^2\Theta}{Kq^2}}\left[\frac{\sin 2\Phi\sin 2\Theta}{4}\left(1 + \sin\frac{\varphi}{2}\right) + \cos\Phi\cos\frac{\varphi}{2}\right]^2 \qquad (9)$$

The orientationally averaged intensity correlation function $\bar{g}_2(t)$ appropriate for a polycrystalline sample may then tentatively be expressed as

$$\bar{g}_2(t) = 1 + \frac{\alpha}{4\pi}\int_0^{\pi}\sin\Theta\,\mathrm{d}\Theta\int_0^{2\pi}\mathrm{d}\Phi\,\exp[-2\Gamma_u(\Theta)t]I^2(\Theta,\Phi) \qquad (10)$$

assuming, as usual, a Gaussian statistics for the randomly scattered field and also an isotropic distribution for the anisotropic domains. In a simple numerical estimate of eq 10, with the rough approximation that the amplitude $I$ of the undulation mode decreases quadratically with $\theta$ as $\theta - \varphi/2$ departs from 0, i.e., as $q_z$ departs from 0, and that it essentially vanishes at $|\theta - \theta_0| \geq 6°$ (from the experimental finding), we found the characteristic relaxation frequency $\bar{\Gamma}_u$ of the orientationally averaged correlation function $\bar{g}_2(t)$. It turns out that $\bar{\Gamma}_u$ is approximately 3 times larger than $\Gamma_u$ taken at $q_z = 0$ in the oriented case.

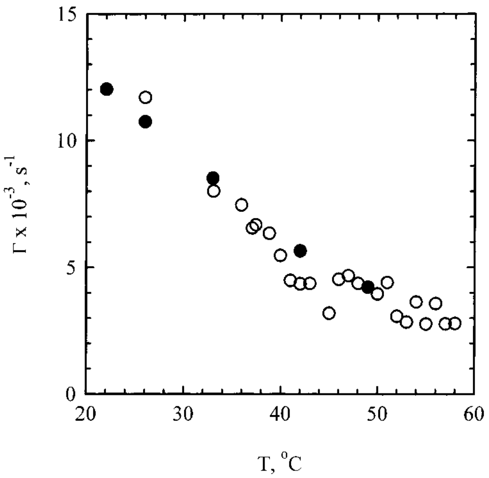

**Figure 7.** Temperature dependence of the relaxation frequency $3\Gamma_u$ (●),where the factor 3 accounts for the averaging over all possible orientations of grains, of the undulation mode compared with the relaxation frequency $\Gamma_f$ (○) of the fast (or "$D_X$") mode reported in a previous work.[15]

This has led us to perform again the measurement of the "fast mode" relaxation frequency $\Gamma_f$, for a *disoriented* sample and in the same temperature range as for measuring $\Gamma_u$ with an oriented sample. Figure 7 shows $3\Gamma_u$ and $\Gamma_f$ together as a function of the temperature. We can thus conclude that in the ordered lamellar block copolymer the fast mode observed on the polycrystalline sample corresponds to the undulation mode averaged over all possible orientations, $\Gamma_f = \bar{\Gamma}_u$.

## Conclusion

The undulation mode—a dynamic attribute of all systems with the smectic A symmetry—has been studied on an *oriented* sample of a diblock copolymer in its lamellar state. The splay modulus $K$ is obtained from the anisotropy of the dispersion relation of this mode, using an extrapolated value for the viscosity in the ordered state. The "fast mode" usually observed in dynamic light scattering with *disoriented* lamellar samples is most probably the counterpart of the undulation mode in the oriented case, averaged over all possible orientations.

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